QUARTERLY PROGRESS REPORT #15

on

ELEVATED TEMPERATURE STRESS CORROSION OF HIGH STRENGTH SHEET MATERIALS IN THE PRESENCE OF STRESS CONCENTRATORS

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by

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ABSTRACT

During this quarterly period, experiments have been carried out by use of each of the techniques that have been developed for studying the mechanism of stress corrosion cracking of titanium alloys. Tests on the hot stage have shown that the diffusion rate of the corrosion products that eventually leads to fracturing is 15 to 40 times as fast in a "wet" atmosphere as in a "dry" one.

A new technique for qualitatively studying the electrochemistry of titanium was also introduced in this period. The procedure consisted of studying the appearance of the titanium under a drop of hot salt. By this simple process it was shown that the previously proposed mechanism for general corrosion as ascertained from the corrosion cell is valid. In these more recent experiments it was shown that the titanium is dissolved only under the salt drop, i. e., this location is an anode. At the periphery of the salt bead and under the spreading corrosion product, the surface is clean, but metal is not dissolved, i. e., a cathode is formed. This corrosion mechanism of titanium under hot salt is identical with that previously described for a water drop on steel. The mechanism consists of an oxygen differential cell with the oxygen being deficient under the drop and available at its periphery.

INTRODUCTION

During this three month period, tests in the oxygen differential cell, as well as, in the tensile hot stage, and X-ray diffraction studies were all continued. A comparison of wet and dry environments in the tensile hot stage was described in the previous quarterly report. During the present period, the experimental procedure was modified to obtain quantitative data on the effect of water vapor on the diffusion of the secondary corrosion product which is thought to cause cracking. Test results are presented both as lapsed time color photographs, and as measured diffusion rates.

Although work on the oxygen differential cell is also continuing, test results obtained by this technique are very slow because the experimental procedures are very cumbersome. To develop qualitative, as compared to quantitative, electrochemical data, a very simple procedure was introduced during this period. The process consisted of placing a very small single drop of salt slurry on an unstressed test sample and observing the corrosion visually. This technique is essentially identical with the classical work done on water drops placed on steel or zinc. Evans showed by the use of pH sensitive gels that the corrosion at the periphery of a water drop is cathodic and that the center is anodic. The steel under the center of the water drop, i.e., at the oxygen deficient anode, is dissolved, whereas, at the periphery of the water drop, i.e., at the oxygen rich cathode, the oxide is removed. Using this single drop procedure, it was shown that under the salt bead titanium is dissolved, i.e., an anode is formed and at the periphery of the drop and under the corrosion product that surrounds the drop, a cathode forms. This result is consistent with the electro-chemical corrosion mechanism tentatively described on the basis of data collected in the differential oxygen cell, but test results are more easily obtained by the drop experiment.

TEST RESULTS

Tensile Hot Stage Experimental Procedures

Two series of experiments were run in the tensile hot stage to determine how water vapor affects the corrosion cracking of titanium by hot sea salt and hot reagent grade sodium chloride. In the wet experiments the hot stage was modified so that water could be intro-

duced into the chamber and a high water vapor content maintained
around the specimen. A schematic diagram of the method of main-
taining a high humidity near the specimen is shown in Fig. 1.

The water content of the air passing through the hot stage
chamber was determined by trapping the water vapor at the exit end
of the hot stage in Drierite ($CaSO_4$) and determining the water vapor-
air ratio by the weight of the water and the weight of the known volume
of air passed through the hot stage chamber. The air flow in all
experiments was obtained by using compressed air flowing at the rate
of 20 to 40 ml/minute.

The dry experiments were run with the apparatus shown in the
schematic diagram of Fig. 2. The compressed air, in this case, was
first passed through a Drierite column which dried it to a dew point
of -100°F prior to passing into the hot stage chamber across the
specimen and then out the exit port through a flow meter.

For the dry test, the sea salt was applied to the specimen in
slurry form and dried for 67.5 hours at 300°F. before the specimen
was loaded and the temperature raised to 650°F. The sea salt for
the wet test was applied this way excepting the pre-drying time was
reduced to 17.5 hours.

The reagent grade sodium chloride for the dry experiment was
vapor deposited on the specimen arms under vacuum after the specimen
was masked to prevent salt from adhering to areas other than the arms.
This specimen was then transferred to the hot stage and run with the
dry air train. A stress of 50,000 psi was maintained for all experiments.

Tensile Hot Stage Results

Wet Experiments - The sea salt and reagent grade sodium
chloride gave results which were almost identical in the wet environment,
and failure occurred in both cases in less than twenty hours. The
specimen with sea salt had a blue surface film form at the salt bead
and within one hour the blue coloration had moved into the stressed area,
Fig. 3. After reaching the stressed area the diffusion rate of the blue
corrosion product decreased very rapidly. The blue area was then
covered with a gray-white film which grew heavier with time, until

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the test was discontinued after ten hours when a crack was observed.

The sodium chloride test progressed in the same manner as the sea salt experiment, except that the sodium chloride interface diffusion rate was somewhat slower. The retarded diffusion was probably caused by a slightly lower water vapor content in the sodium chloride test. Measurement of the water vapor exiting the hot stage chamber gave an average of 2.8 part of water/100 part air in the sea salt experiment and 1.8 part water/100 part air in the sodium chloride run. In both experiments, the appearance and generation of the corrosion products were nearly identical, the main difference being the diffusion rate.

Dry Experiments - In contrast to the wet experiments, the tests run with the sea salt specimens as dry as possible required much more time for the corrosion products to form, diffuse to the stressed area and cause failure. The time required to form the first detectable crack in the dry test was about 152 hours as compared with ten hours in the wet test. The time lapse photographs of the dry experiment are seen in the right of Fig. 3.

A very dry vapor deposited sodium chloride experiment was run, but the results were not conclusive, because the salt deposit was extremely thin (about .00075") and all the salt appeared to have been consumed without forming enough corrosion product to allow diffusion. The time that this experiment ran was 200 hours.

Diffusion Rate Measurements

The diffusion rate of the corrosion products were measured on the wet and dry sea salt experiments, Fig. 4a and 4b. It is apparent that water vapor greatly accelerates the movement of the corrosion products, and is probably essential in causing cracking. (Note that the abscissa scales in Fig. 4 differ by a ratio of 40.1).

Corrosion Cell

A series of experiments have been conducted in the argon atmosphere hot corrosion cell to determine the effects of various

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salts on the cracking of Ti-6Al-4V and the Ti-8Al-1Mo-1V.

In the experiments conducted on the 6Al-4V alloy there appears
to be little difference in the cracking mechanism if a stressed sample
is subjected to a sea salt or a KCl-LiCl eutectic salt environment at
elevated temperatures. A sea salt experiment in which two samples
were stressed to 77,000 psi was conducted at 800°F under a purified
argon atmosphere for nine hours. As previously described, both
specimens were in contact with a sea salt bridge, but one was electri-
cally coupled to an external Ti-6Al-4V titanium electrode which was
also in contact with the air exposed end of the salt bridge. On removal
of the stressed specimens from the argon chamber, the coupled sample
cracked in two within one hour at ambient temperature and 100 percent
relative humidity while the uncoupled sample did not crack even though
held under stress for 60 hours. In another experiment Ti-6Al-4V was
held in contact with the KCl-LiCl eutectic salt at 600°F for five hours.
The results were similar to those obtained with sea salt experiments
and of those previously reported with KCl-LiCl. The difference in time
of exposure is attributed to the different ionic conductivities of the
two salts.

Five sea salt and four NaCl salt experiments have been con-
ducted on the Ti-8Al-1Mo-1V alloy. The cracking results are quite
scattered ranging from both samples cracking to neither cracking.
At this time, it is felt that the major variable affecting cracking for
a fixed time exposure is the water of hydration in the salt. In some
cases, relatively large amounts of water is seen being driven off from
the salt even though the salt was previously dried at 300° for twelve
hours.

Examination of the external electrodes indicates that the
Ti-8Al-1Mo-1V alloy undergoes grain boundary attack when in contact
with chloride salts at elevated temperatures.

X-ray Investigation

A Debye Scherrer X-ray photograph was taken of the corrosion
product formed from the exposure of Ti-6Al-4V alloy in the KCl-LiCl
eutectic corrosion cell, and only KCl, LiCl, and TiO_2 (Anatase) were
detected.

Salt Drop Experiments

In a number of previous reports (see for example Ref. 1) it was proposed that the titanium alloys in the presence of hot salts undergo stress corrosion cracking in two steps. The first step is the dissolution of titanium under the salt by an electrochemical mechanism associated with an oxygen differential cell. The area under the salt is an anode due to the oxygen deficiency, and at the periphery of the bead, where more air is available, a cathode is developed. If such a situation exists it would be identical to the corrosion of steel or zinc under a salt water drop. Hence, several experiments were conducted to determine if a salt drop on the Ti-8Al-1Mo-1V alloy, heated in the 650 to 800°F range would give results analogous to the water drop experiment on steel as described by Evans (2). This author showed that anodic region developed under the center of the water drop where oxygen was deficient and that dissolution of the metal occurred only in this area. Near the outer edge of the water drop where there was a higher oxygen concentration, the metal was clean, bare and unattacked. The salt drop experiments conducted on Ti-8Al-1Mo-1V alloy indicated that the attack by hot salt is identical to Evans' experiment with steel as can be seen by comparing the two photomicrographs in Fig. 5. It is apparent that the two types of corrosion result from the same mechanism.

The photomicrograph in Fig. 5a was obtained as follows: The salt slurry was placed on the sample and then dried over night at 300°F in an attempt to have the slurry as dry as possible. The specimen was then heated to 800°F and the attack allowed to proceed for five hours. At the end of this time, the specimen was washed in distilled water and photographed. Unfortunately, with this specimen it was not possible to relate the size of the attack areas with the size of the original salt drop. In a second salt drop experiment a drop of salt was placed on the specimen and heated immediately to 800°F. Corrosion occurred rapidly and from about one-half to seven minutes at temperature the sample had the appearance shown in Fig. 6a. The specimen was then held at temperature for 32 minutes, cooled and washed in distilled water, after which it had the appearance shown in Fig. 6b. The metal under the bead is obviously dissolved and the

anode appears to expand and eventually cover an area larger than
the size of the original salt spot, compare Figs. 6a and b. The
gray spotty area between the bead and unattacked region in Fig. 6b
appears to be converting from a cathode to an anode. Examination
in this region indicates that the grain boundaries are attacked and
a few of the grains completely dissolved, Fig. 6c. From this it
must be assumed that the dissolution under the salt bead starts
at the grain boundaries which is the most anodic portion of the
metal and then proceeds over the entire grain.

Similar tests made with reagent grade sodium chloride have
an identical appearance indicating that this salt and sea salt cause
corrosion by identical mechanisms.

FUTURE WORK

The hot stage will be used to study the salt drops to determine
how changes in water vapor content and atmospheres affect the
formation of the salt drop attack on the Ti-8A1-1Mo-1V alloy. Also
efforts will continue to produce a completely dry salt in order to
determine if a completely dry system will cause the titanium to
corrode and crack.

Work will be continued on the X-ray study to determine the
composition of the intermediate corrosion products and, in turn,
will lead to the identification of this chemical reaction involved in
the corrosion of titanium.

REFERENCES

1. Kirchner, R. L., and Ripling, E. J., Elevated Temperature Stress Corrosion of High Strength Sheet Materials in the Presence of Stress Concentrators, Materials Research Laboratory, Inc., Richton Park, Illinois, November, 1964.

2. Evans, U. R., The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications, pp 115-121, Edward Arnold (Publishers) Ltd., London, 1960.
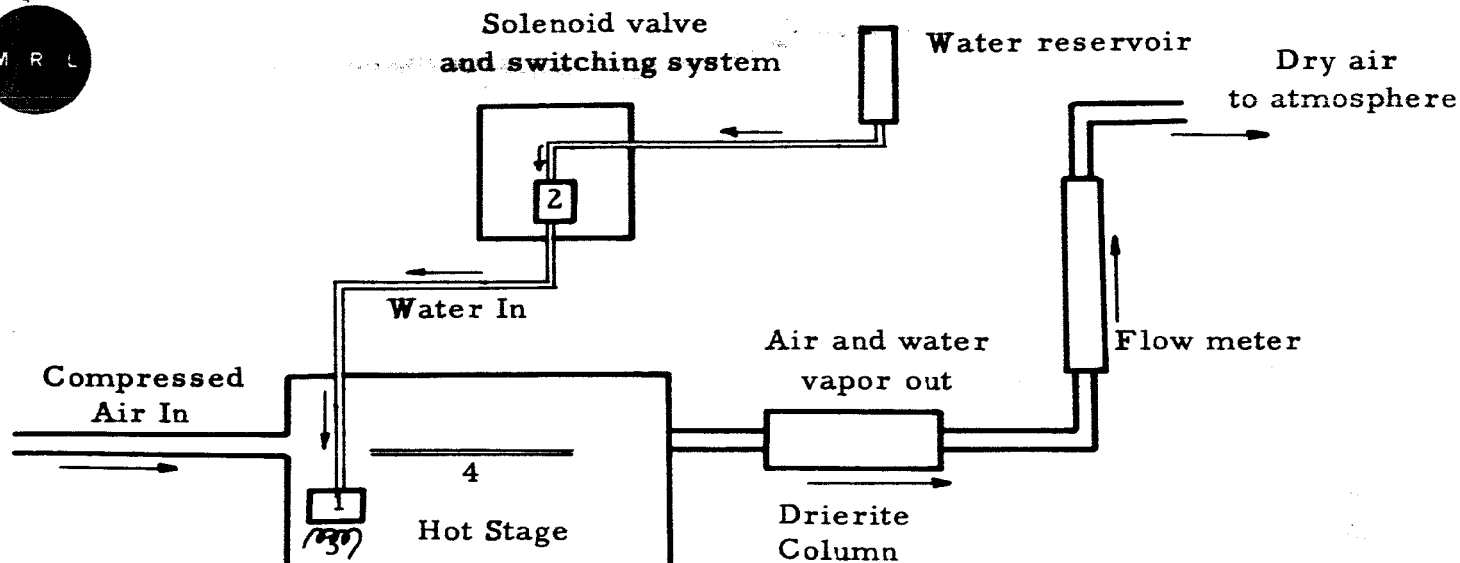
Solenoid valve
and switching system

Water reservoir

Dry air
to atmosphere

2

Water In

Compressed
Air In

Air and water
vapor out

Flow meter

4

Hot Stage

Drierite
Column

Fig. 1 SCHEMATIC DRAWING OF TENSILE HOT STAGE
FOR HIGH HUMIDITY EXPERIMENTS.

(1)   Water container in hot stage chamber.
(2)   Solenoid valve to maintain a given water level in container (1).
(3)   Water container heating coil.
(4)   Specimen

Air to
atmosphere

Flow meter

Drierite
Column

Compressed
Air In

Air with dew
point of -100F

Specimen
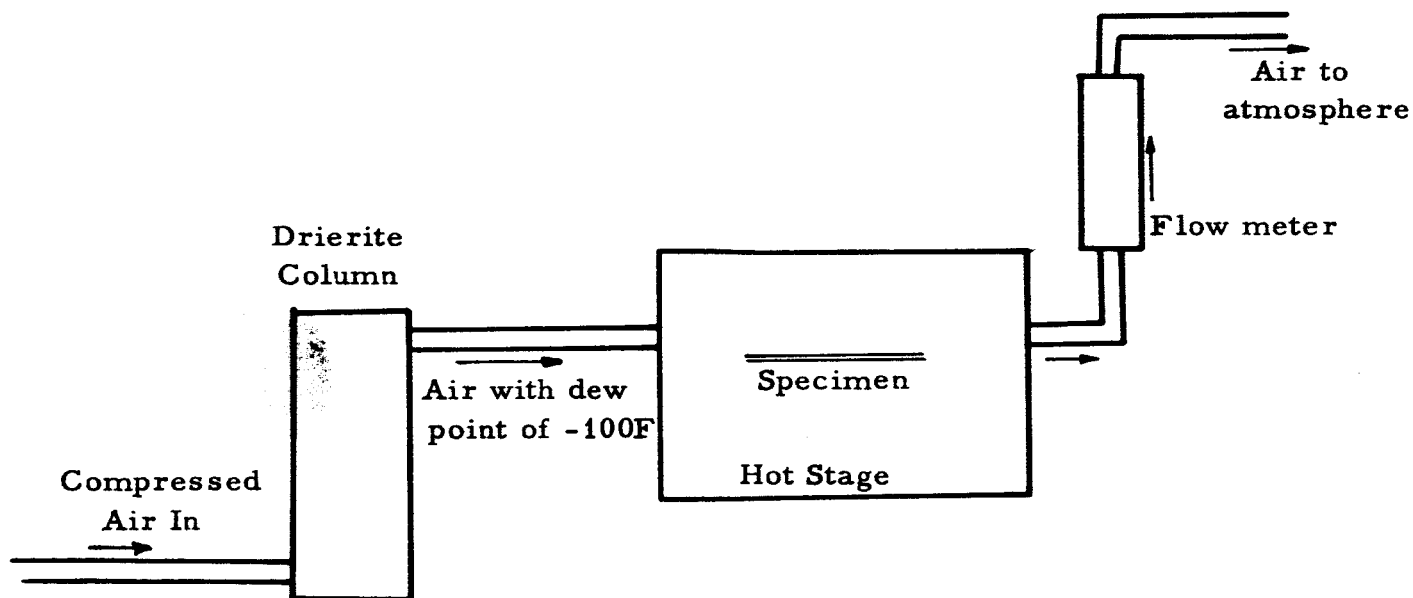
Hot Stage

Fig. 2   SCHEMATIC DRAWING OF TENSILE HOT STAGE
AND AIR DRYING TRAIN.
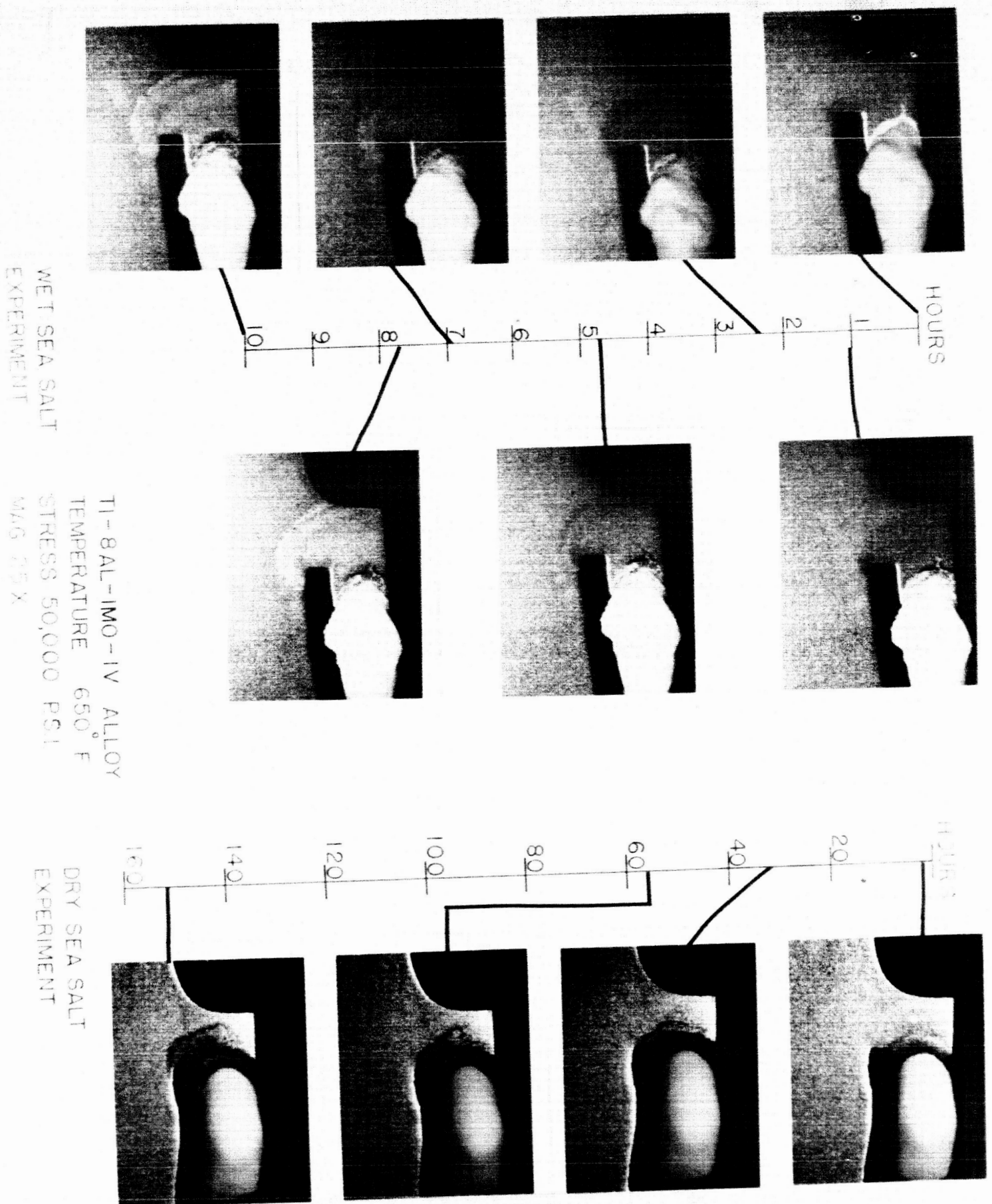
Fig. 3 DIFFUSION OF CORROSION PRODUCT IN WET AND
DRY TEST. (Photographs reduced approximately
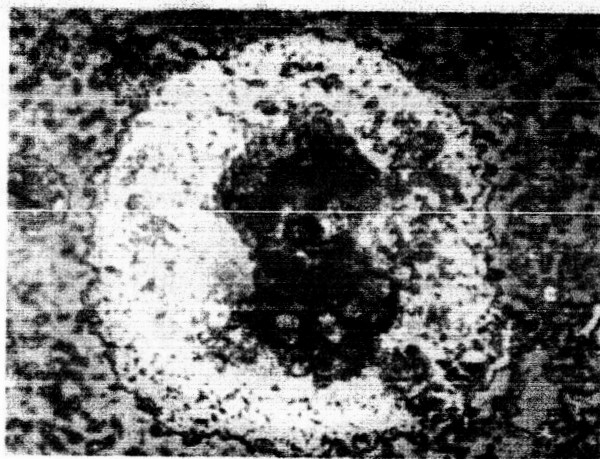one-half in reproduction.)
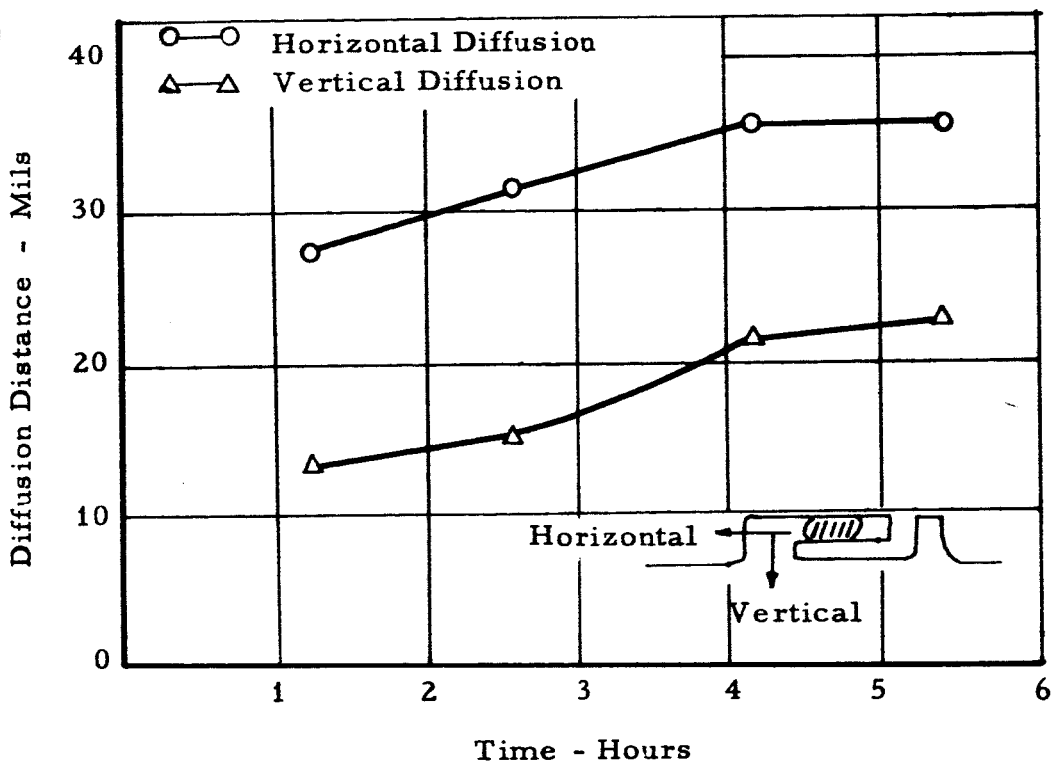
(a)
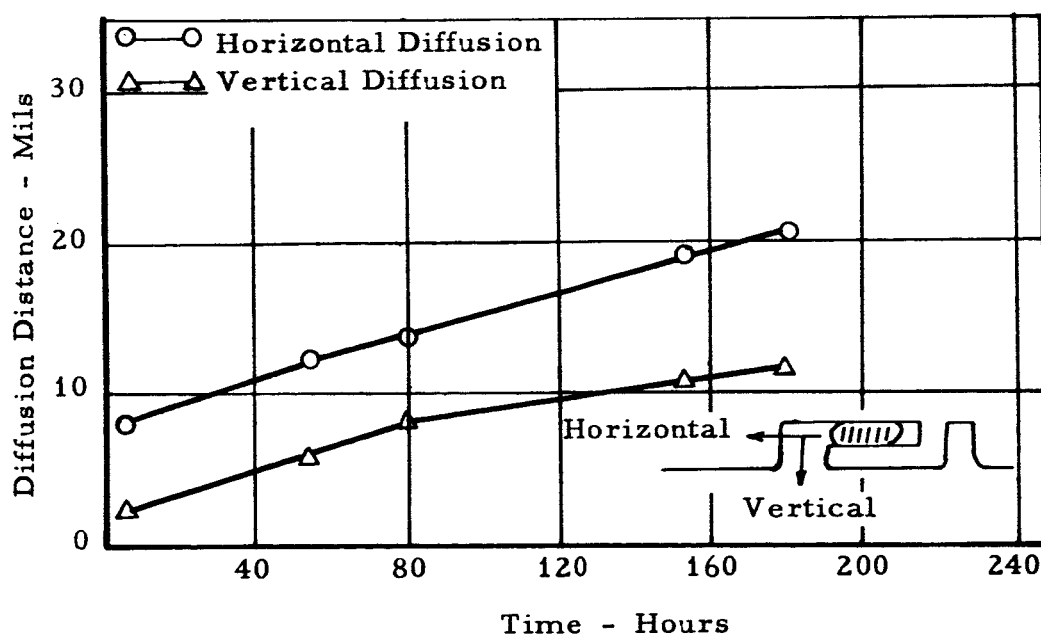
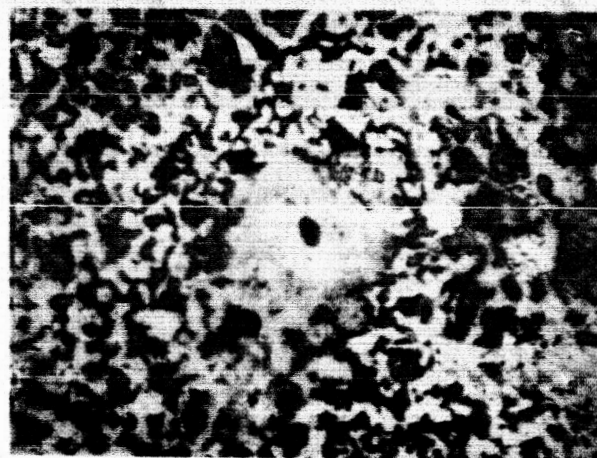(b)

Fig. 4   THE DIFFUSION RATE OF THE CORROSION
         PRODUCTS AS A FUNCTION OF TIME.

         (a)   Wet sea salt experiment.
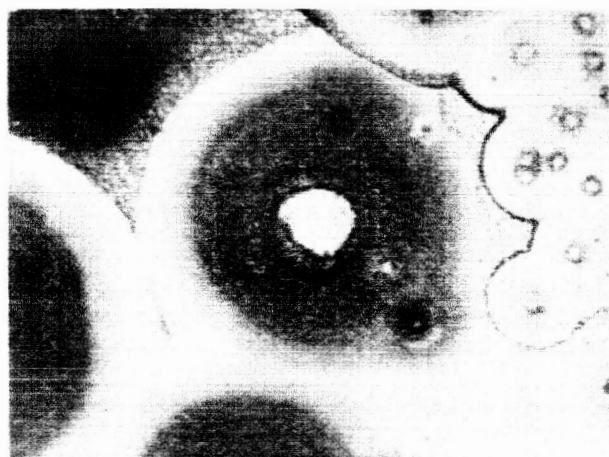   (b)   Dry sea salt experiment.

SEA SALT ON Ti-8Al-1Mo-1V
at 800°F FOR FIVE HOURS.
MAG. 260X.

(b)

Fig. 5

3% NaCl SOLUTION ON
STEEL PLATE AT
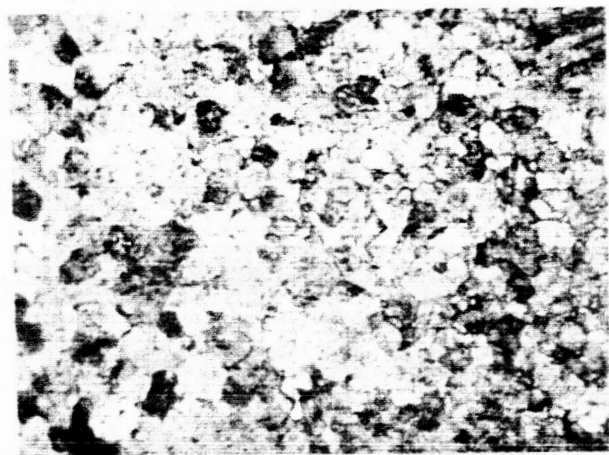AMBIENT TEMPERATURE.
MAG. 260X.

SEA SALT ON Ti-8Al-1Mo-1V
AT 800°F FOR SEVEN MINUTES.
MAG. 25X.

(b)

SEA SALT ON Ti-8Al-1Mo-1V
AT 800°F FOR 32 MIN.
WASHED SURFACE.
MAG. 25X.

(c)

GRAIN BOUNDARY ATTACK
IN ANODIC REGION ON
Ti-8Al-1Mo-1V.
MAG. 520X.

Fig. 6

Fig. 5 - COMPARISON OF CORROSION OF
TITANIUM UNDER HOT SALT BEAD
AND STEEL UNDER SALT WATER
DROP.

Fig. 6 - FORMATION OF A
CORROSION PIT IN
TITANIUM.